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PROCESS FOR PRODUCING GASOLINE FROM A CRACKED FEED STOCK BY CATALYTIC HYDROCRACKING

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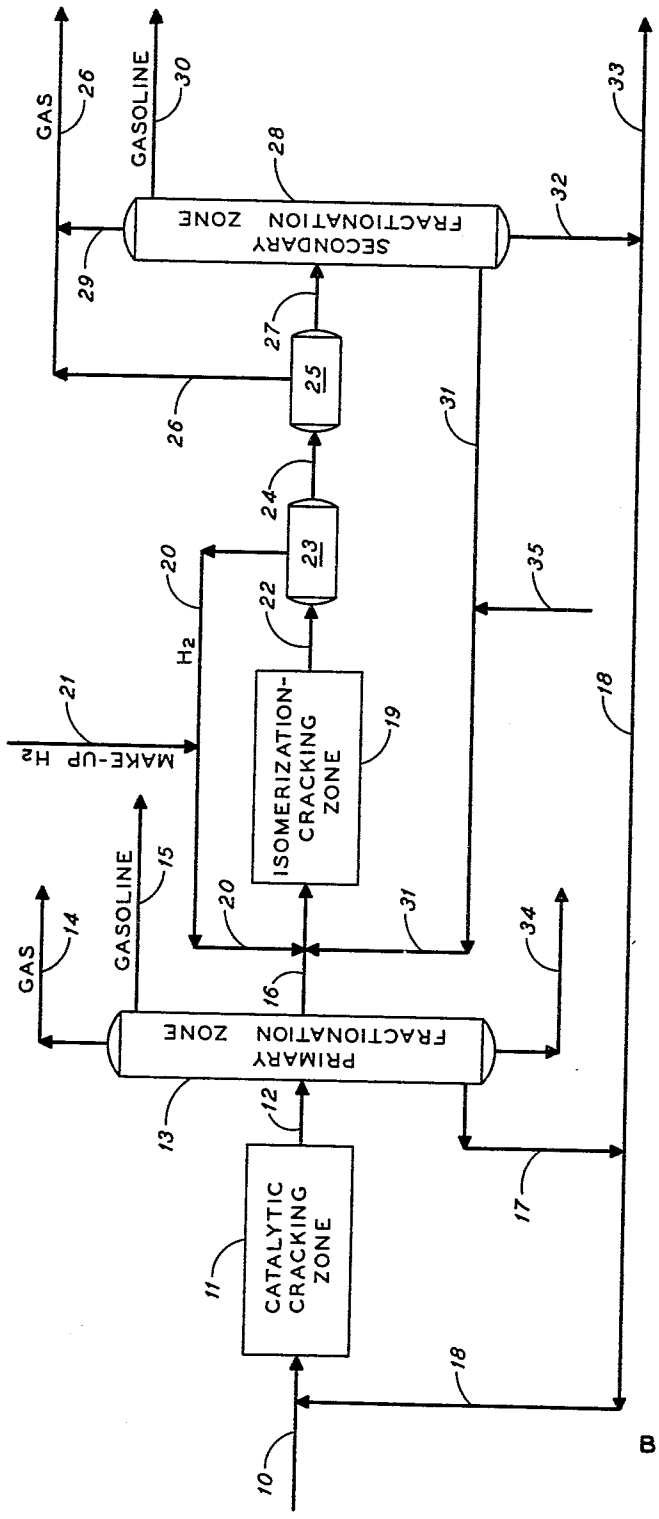

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PROCESS FOR PRODUCING GASOLINE FROM A CRACKED FEED STOCK BY CATALYTIC HYDROCRACKING

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This invention relates to a catalytic process for producing high quality gasoline from comparatively high-boiling hydrocarbon fractions, and it is particularly directed to an integrated process involving a novel sequence of operating steps for producing high octane gasoline from petroleum stocks having an initial boiling point above about 325° F. and an end point below about 900° F.

This application is a continuation-in-part of our co-pending application Serial No. 575,254, filed March 30, 1956, now abandoned.

ISOMERIZATION-CRACKING STEP

The process of the present invention includes an isomerization-cracking step wherein a hydrocarbon stock having an initial boiling point above about 325° F. and an end point below about 900° F. is contacted in an isomerization-cracking zone, in the presence of from about 1,500 to 30,000 s.c.f. H_2 per barrel of total feed to said zone, with a catalyst composite comprising a hydrogenating-dehydrogenating component and an active cracking support. This contacting step is conducted at a temperature of from about 400° to 900° F., a pressure of at least 500 p.s.i.g., and an LHSV of from about 0.2 to 15. The effluent from the isomerization-cracking zone is then preferably freed of a hydrogen-rich recycle stream which is returned, along with make-up hydrogen to replace that consumed in the reaction, to that zone. The remaining portion of the effluent is then separated so as to recover a gas fraction, at least one gasoline fraction, an intermediate fraction boiling above the heaviest gasoline fraction, having an initial boiling point of about 375°±50° F., and an end point of about 475°±25° F., and a bottoms fraction boiling above said intermediate fraction. A portion, and preferably all, of the intermediate fraction recovered from the isomerization-cracking zone is returned to that zone.

CATALYTIC CRACKING STEP

A preferred manner of operation is to integrate a catalytic cracking step with the isomerization-cracking step referred to above. It has been found that, if particularly well-defined boiling range fractions are employed as feed and recycle streams, the combined process affords a means of producing an excellent high quality gasoline that will meet all of the requirements of the present-day, high compression, internal combustion engine.

FEED

The present invention is directed to the conversion of gasoline of straight-run, thermally cracked and, preferably, catalytically cracked, hydrocarbon fractions having initial T.B.P.'s (true boiling point) of above about 325° F. and end points of below about 900° F. Among the fractions falling within this general range will be found those hydrocarbons which are known in the refining art as naphthas, gas oils, coker distillates, and cracked (thermally or catalytically) cycle oils. In any case, the feed, along with from about 1,500 to 30,000, and preferably from about 3,000 to 15,000 s.c.f. (standard cubic feet) of hydrogen per barrel of total reaction feed, is

passed into the isomerization-cracking zone at an LHSV (liquid hourly space velocity) of from about 0.2 to 15, and preferably from about 0.4 to 3.0, and intimately contacted with the catalyst.

NITROGEN CONTENT OF FEED

While the invention can be practiced with utility in connection with petroleum feeds to the isomerization-cracking zone containing relatively large quantities of nitrogen, the operation becomes much more economical with stocks containing less than 200 p.p.m., preferably below 100 p.p.m., and much more preferably below 10 p.p.m., of nitrogen. A reduction in feed nitrogen level permits the isomerization-cracking reaction to be conducted at lower temperatures than with feeds containing relatively large amounts of nitrogen compounds. Therefore, in the case of feed stocks which are not inherently low in nitrogen, acceptable levels can be reached by pretreating the feed to the catalytic cracking unit by a nitrogen compound extraction process, or by contacting either the catalytic cracking unit feed or, preferably, the particular feed to the isomerization-cracking process with hydrogen in the presence of a suitable catalyst at elevated temperatures and pressures to remove nitrogen compounds therefrom. A particularly effective catalyst for removing nitrogen by hydrogenation is one wherein a co-precipitated molybdena-alumina material (e.g., one prepared in accordance with the disclosure of U.S. Patent No. 2,432,286 to Claussen et al., or U.S. Patent No. 2,697,006 to Sieg) is combined with cobalt oxide, the final catalyst having a metals content equivalent to about 2% cobalt and 7% molybdenum. Representative processing conditions for removing nitrogen with this catalyst are an LHSV of 1–3, 700°–800° F., 200–1500 p.s.i.g., and 1000–15,000 s.c.f. H_2 per barrel of feed stock.

OPERATING CONDITIONS

The contacting step is conducted under a pressure of at least 500 p.s.i.g., and preferably from about 800 to 3,000 p.s.i.g. The temperature is maintained in the range of from about 400° to 900° F., preferably from about 500 to 800° F., because, at temperatures above about 800° F., the amount of gasoline product lost to the less desirable C_3 and lighter materials rapidly increases, thus lowering the motor fuel yield. For example, it has been found that the amount of methane produced at 800° F. per unit of converted product is approximately sixteen times as great as that formed at 700° F., and four times as great as that produced at 750° F. At higher temperatures the situation becomes much worse. Accordingly, resort is normally had to temperatures above about 750° F. only in the last stages of the catalyst on-stream period when it is desired to maintain relatively high activity at the expense of higher light gas losses or, in the case when the relatively high nitrogen-containing feeds are processed. Further, operations at temperatures above about 750° F. and at low or moderate pressures induce a relatively rapid decrease in the activity of the catalyst as reflected by reduced per-pass conversion levels. Thus, when operating at 875° F. and at a relatively low pressure, for example 1500 p.s.i.g., on a hydrofined light cycle oil feed, regeneration of a cobalt-molybdenum on silica-aluminum catalyst is required in most instances after on-stream periods of one day or less, which contrasts with on-stream periods of 100 to 300 or more hours at good activity as temperatures are maintained below about 825° F. With operation at 800° F. and higher with the same and similar feeds, but with nickel sulfide on silica-alumina, regeneration is required after on-stream periods of a few hundred hours or less, compared with operation below 700° F., with which can be obtained on-stream periods of several thousand hours without regeneration. In

the present process, it is recommended that the reaction be conducted at an initial on-stream temperature from about 550° to 650° F., with a progressive increase to about 750° to 850° F., so as to maintain catalyst activity at a controlled level. The initial and terminal temperatures will vary, with character of feed and catalyst, within the over-all range specified above.

CATALYST, GENERAL

The catalyst employed in the isomerization-cracking zone is one wherein a material having hydrogenating-dehydrogenating activity is deposited or otherwise disposed on an active cracking catalyst support. The cracking component may comprise any one or more of such acidic materials as silica-alumina, silica-magnesia, silica-alumina-zirconia composites, alumina-boria, fluorided composites, and the like, as well as various acid treated clays and similar materials. The hydrogenating-dehydrogenating components of the catalyst can be selected from any one or more of the various groups V, VI, VII and VIII metals, as well as the oxides and sulfides thereof, alone or together with promoters or stabilizers that may have by themselves small catalytic effect, representative materials being the oxides and sulfides of molybdenum, tungsten, vanadium, chromium, and the like, as well as of metals such as iron, nickel, cobalt, and platinum. If desired, more than one hydrogenating-dehydrogenating component can be present, and good results have been obtained with catalysts containing composites of two or more of the oxides of molybdenum, cobalt, chromium, and zinc, and with mixtures of said oxides with fluorine. The amount of the hydrogenating-dehydrogenating component present can be varied within relatively wide limits of from about 0.5 to 30% based on the weight of the entire catalyst.

AROMATICS CONTENT OF FRACTION RECYCLED TO ISOMERIZATION-CRACKING STEP

The amount and nature of the catalyst hydrogenating-dehydrogenating component and the catalyst support in a preferred embodiment of the process of the present invention should enable the resulting catalyst composite to effect the production in the isomerization-cracking zone at reaction conditions of a product such that the intermediate boiling range fraction to be recycled in whole or in part as aforesaid will still have a relatively high aromatic content compared with the aromatic content of the original feed. Where said intermediate boiling range fraction is relatively aromatic, it is an excellent recycle stock for the isomerization-cracking zone, and contributes to an increased production of the desired gasoline fraction. This is somewhat unexpected; heretofore the emphasis has been on avoiding the production of an aromatics-rich fraction in said boiling range because it has been felt that fractions in said boiling range were best usable directly as fuels and fuel blending stocks without recycling them. Therefore, aromatics-free fractions in said boiling range were sought, because an aromatics-rich fraction in said boiling range is undesirable for such fuel uses as diesel fuels, jet fuels, and blending stocks therefor. Accordingly, heretofore a catalyst, for example platinum on silica-alumina, has been used having an extremely high aromatics-saturation activity, which has resulted in the production of non-aromatic products in said boiling range rather than a recycle stock.

In addition to the foregoing reason for previous avoidance of the production of aromatics-rich stocks in said boiling range, it has not been appreciated heretofore just how, even had they been desired, aromatics-rich stocks in said boiling range could have been produced efficiently and with predictability in a hydrocracking process from feeds such as those used in the process of the present invention.

CATALYST CHARACTERISTICS REQUIRED TO ACHIEVE AROMATICS-RICH RECYCLE FRACTION

It has now been found that in order to achieve the desired production of the aromatics-rich intermediate fraction to be recycled, at sustained required conversion levels, the catalyst used must have certain particular and unique characteristics for the purpose intended, relating to (*a*) cracking activity, (*b*) "severity factor," or SF, as discussed below, and (*c*) activity in influencing ratio of iso to normal C_4–C_5 paraffins. More particularly, it has been found that the catalyst used must have either or both of the following satisfactory charactertics:

(1) SF, as defined below, less than 2.0.
(2) A "cracking activity index," or CAI, as defined below, of at least 50, and an iso/normal C_4–C_5 paraffin production "iso normal activity index," or INAI, as defined below, of more than 1.

The severity factor, SF, is a measure of the balance between cracking reactions, including disproportionation, and aromatics hydrogenation. It is determined by subjecting the catalyst to a standard test wherein a trimethyl benzene feedstock is passed over the catalyst at 2.0 LHSV, 1200 p.s.i.g., 9000 s.c.f./bbl. hydrogen rate, and 650° F. block temperature. The severity factor is defined in terms of the products produced under such conditions, as follows:

$$SF=\frac{\text{aromatics hydrogenation index}}{\text{aromatic cracking index}}$$

where

$$\text{aromatics hydrogenation index}=\frac{\text{aromatics converted minus aromatics in synthetic product}^1}{\text{aromatics converted}}$$

and where

$$\text{aromatics cracking index}=\frac{\text{aromatics in synthetic product}^1}{\text{aromatics in feed }(A_f)}(A_p)$$

It can be shown that

$$SF=\frac{A_f}{A_p}-1$$

where this is a high value the catalyst has a high selectivity for aromatics saturation. Accordingly, the preferred catalysts for use in the process of the present invention are those having the lower severity factors, and if their severity factors are low enough, i.e., less than 2.0, they will be satisfactory regardless of their cracking activity indices, or CAI, and regardless of their iso/normal activity index, or INAI.

The cracking activity index, CAI is the volume percent conversion of a light cycle oil feed converted by the catalyst to products boiling below feed initial boiling point at conditions of: 2.0 LHSV, 1200 p.s.i.g., 6500 s.c.f./bbl. gas rate, and temperature below 630° F., once-through operation.

The iso normal activity index, INAI, is the iso/normal ratio of C_4–C_5 paraffins produced with the catalyst when a normal decane feed is used, compared with the thermodynamic equilibrium iso/normal ratio of C_4–C_5 paraffins, which latter ratio is multiplied by a factor which produces a result of 1. The iso/normal ratio of C_4–C_5 paraffins actually produced over a given catalyst is multiplied by this same factor to obtain the INAI of the catalyst.

[1] Synthetic product is product boiling below initial boiling point of feed.

EXEMPLARY CATALYSTS

Exemplary catalysts having satisfactory characteristics as aforesaid include those containing: (*a*) about 1 to 12% molybdenum oxide, (*b*) a mixture of from 1 to 12% molybdenum oxide and from 0.1 to 10% cobalt oxide, (*c*) mixtures of from about 0.5 to 10% each of cobalt oxide and chromium oxide, (*d*) 0.1–10% nickel, oxide or nickel sulfide, (*e*) 0.1–10% cobalt, cobalt oxide, or cobalt sulfide, (*f*) mixtures of from 0.1 to 10% each of nickel and cobalt, as metal, oxide or sulfide, in each case the said hydrogenerating-dehydrogenating component being deposited on an active cracking support, comprising silica-alumina beads having a silica content of about 70 to 99%, the metal content on the support being adjusted within the aforesaid ranges as required by some preparative methods to obtain satisfactory SF values. Thus, the molybdenum oxide catalyst can be prepared readily by soaking the beads in a solution of ammonium molybdate, drying the catalyst for 24 hours at 220° F., and then calcining the dried material for 10 hours at 1000° F. If cobalt oxide is also to be present, the calcined beads can then be similarly treated with a solution of a cobalt compound, whereupon the catalyst is again dried and calcined. Under favorable operating conditions the isomerization-cracking catalyst will maintain high activity over periods of 50 to 300 or more hours. The activity of the used catalyst can then be increased, if desired, by a conventional regeneration treatment involving burning off catalyst contaminants with an oxygen-containing gas.

TYPES OF OPERATION TO WHICH PROCESS IS ADAPTED

While the invention will be described more particularly in connection with the method of fixed catalyst bed operation wherein the respective catalyst beds are periodically regenerated in situ, the process is also well adapted to be carried out in a moving catalyst bed, or in a slurry-type reaction system, or in one of the fluidized catalyst type. In the latter methods of operation (wherein the general procedures to be employed are now well established in the art), separate vessels are employed for the respective reaction and regeneration zones. However, since in carrying out the process of this invention the catalyst retains its activity over long periods of time, it is normally preferable, from an economic standpoint, to employ the fixed catalyst bed method of operation or some modification thereof.

EXAMPLES

Extensive experimental data covering variations in feed composition, catalysts, and operating variables have been utilized in the development of plant process designs incorporating the inventive features of the subject process. In the following case examples and detailed description of a preferred embodiment of the present invention, the operating variables and conversion factors have been determined by correlation of experimental data and projected for full-scale plant operations in accordance with the specific process design and feed composition. Thus, in the following cases examples, the results that can be expected from a 10,000 b.p.d. (barrels per day) isomerization-cracking zone under the specified operating conditions are shown in Table I. For comparative purposes only, case I shows an isomerization-cracking operation wherein the total bottoms fraction (i.e., that fraction boiling above the gasoline end point) and boiling in the range of from about 400° to 570° F. is recycled to extinction. Case II shows an operation in accordance with the present invention, wherein only the portion of the bottoms fraction boiling from about 400° to 475° F. is recycled to extinction, with the remainder (boiling above about 475° F.) being withdrawn from the system.

	Case I	Case II
Catalyst, 1-5% Molybdenum Oxide on Silica-Alumina.		
Fresh Feed, 400° to 570° F., Hydrofined Catalytically Cracked Cycle Oil, b.p.d.	5,000	6,66
Recycle, b.p.d.	5,000	3,340
Total Feed (including recycle) b.p.d.	10,000	10,000
LHSV	2	2
Temperature, ° F.:		
Initial On-Stream	700	700
Final On-Stream	825	825
Pressure, p.s.i.g.	1,50	1,500
H_2, s.c.f./b. of Total Feed	6,000	6,000
H_2 Consumption, s.c.f./b. of Total Feed	1,300	870
Products:		
Gasoline, C_5+, b.p.d.	5,000	4,440
F-1 Clear	85	88
F-1+3 ml. TEL	95-97	96-98+
Diesel Fuel, b.p.d.	0	2,220
Cetane No.		48

From the above summary it can be seen that the present invention (case II) can be expected to produce gasoline of higher octane number than could be expected by merely recycling the total bottoms fraction to extinction. In the light of current estimates on the millions of dollars of capital investment required to raise present-day premium motor fuels one F–1 octane unit, the high octane gasoline product of the present invention is an extremely advantageous result. Furthermore, it should be noted that the non-recycled portion of the isomerization-cracking unit bottoms (boiling above about 475° F.) can be expected to be an excellent diesel fuel of high cetane number.

OPERATION WITH CATALYTIC CRACKING STEP, GENERAL

As noted hereinbefore, a preferred embodiment of the present invention provides for the integration of a catalytic cracking unit with an isomerization-cracking process. On first considering the combination of these two specific units, it appeared that the catalytic cracking unit should act as the source of the preferred isomerization-cracking unit feed, namely, cracked cycle oil, and that operations should be conducted so as to recycle all of the portions of the effluent boiling above about 325° F. from the isomerization-cracking zone either to that zone (extinction recycle) or to the catalytic cracking unit for further cracking. However, it was discovered that if the process combination were operated according to the method outlined below, and shown in the appended drawing, considerable advantages could be expected over the possible recycle systems initially considered.

According to this preferred embodiment, a hydrocarbon fraction suitable for use as a feed stock to a catalytic cracking unit (such as, for example, a straight-run distillate in the nature of gas oil obtained from crude petroleum by simple distillation) is contacted in a cracking zone with an active cracking catalyst under conditions adequate to effect substantial cracking of the feed. The resulting effluent is passed into a separation zone from which is recovered a gas fraction, a gasoline fraction, an intermediate fraction having an initial boiling point of about 375°±50° F., and an end point of below about 900° F., and a heavy bottoms fraction. The intermediate fraction comprises the fresh feed to an isomerization-cracking unit of the type hereinbefore described. The conditions maintained in the latter unit are also the same as those previously described. The effluent from the isomerization-cracking zone is then freed of a hydrogen-rich recycle stream which is returned, along with make-up hydrogen to replace that consumed in the reaction, to the isomerization-cracking zone. The remaining portion of the effluent is then separated so as to recover a gas fraction, at least one gasoline fraction, an intermediate fraction having an initial T.B.P. of about 375°±50° F., and an end point of about 475°±25° F., and a bottoms fraction boiling above said intermediate fraction.

At least a portion, and preferably all, of the intermediate fraction recovered from the effluent of the isomerization-cracking zone desirably is recycled to that zone, since its high aromatic content makes it very refractory to catalytic cracking. Furthermore, it has been found that, despite its refractory nature to catalytic cracking, this intermediate fraction is readily converted in the isomerization-cracking zone to high octane gasoline boiling below the initial point of the recycle fraction.

Regardless of the amount of the intermediate fraction recovered from the isomerization-cracking zone that is recycled to that zone (as outlined above) it is desirable to recycle at least a portion of the heavy bottoms fraction (having an initial T.B.P. of about 475° ±25° F.) recovered from the isomerization-cracking zone effluent to the catalytic cracking zone. It has been found that this fraction is less refractory in catalytic cracking than conventional light catalytic cycle oil and is more refractory than such cycle stock in the isomerization-cracking reaction. Thus, increased throughput may be attained in both the catalytic cracking and the isomerization-cracking units. Further, by recycling the intermediate cut recovered from the isomerization-cracking zone back to that zone, the aromatics that are so refractory toward further catalytic cracking are, instead, converted to high octane gasoline in the isomerization-cracking zone.

OPERATION WITH CATALYTIC CRACKING STEP, DETAILED DESCRIPTION

As noted above, the following detailed description of a preferred embodiment of the subject invention employs operating variables and conversion factors that have been determined by correlation with experimental data and projected for full-scale plant operations in accordance with the specific process design and feed composition. For comparative purposes only, the advantages of the subject process are demonstrated for processing an increment of light straight-run gas oil through a catalytic cracking unit in a large refinery running mixed California crude oils, with a common light cycle oil stream from all catalytic cracking in the refinery.

Referring to the figure of the appended drawing, which is a simplified flow scheme of a refinery unit suitable for use in practicing the invention, 10,000 b.p.d. (barrels per day) of straight-run light gas oil feed are passed by line **10** into catalytic cracking zone **11** wherein it is contacted, under cracking conditions, with a cracking catalyst. Although the present description is concerned with the cracking of a particular gas oil fraction (light gas oil), the subject process can employ as the feed to the catalytic cracking unit any hydrocarbon fraction that lends itself to the catalytic cracking operation such as heavy gas oil, heavy hydrocarbons derived from oil shale or tar sands, or synthetic fuel processes, and the like. The catalytic cracking reaction may be performed in any particular unit or process directed to that end. For example, it may be done in any of the conventional processes such as the fixed catalyst bed operation of the Houdry commercial units, or the Thermofor or fluid-type moving catalyst processes.

The effluent from catalytic cracking zone **11** is removed therefrom by line **12** from which it is passed into primary fractionation zone **13** wherein it undergoes separation into various boiling range fractions. As shown in the drawing, a normally gaseous (C_3's, C_4's, and lighter) fraction is recovered by line **14**, a gasoline fraction having an initial T.B.P. of about 60° F. and an end point of from about 325° to 425° F. is recovered as a product by line **15**, an intermediate fraction having an initial T.B.P. of above about 325° F. (depending upon the cut point of the gasoline) and an end point below about 650° F. is recovered from zone **13** by line **16**, a bottoms fraction, boiling above said intermediate fraction and normally termed "heavy cycle oil," is recovered by line **17** from which it is preferably returned by lines **18** and **10** to the catalytic cracking zone **11** as a component of the feed, and a tar bottoms fraction (amounting to about 500 b.p.d.) is recovered and passed from the system by line **34**. By employing the noted stock as a feed to a fluid-type cracking unit, employing a silica-alumina catalyst, a gasoline production and recovery of about 3,500 b.p.d. (based on about a 400° F. end point product) can be expected to be recovered from separation zone **11** by line **15**.

The intermediate fraction recovered from separation (or fractionation) zone **13**, amounting to about 4,500 b.p.d., comprises a major proportion of the feed to the isomerization-cracking zone **19**. This intermediate fraction is supplied to the latter unit through line **16**, along with a hydrogen-rich gas stream supplied through line **20**, the latter stream (which includes both make-up hydrogen entering the system by line **21** as well as recycle hydrogen from line **20**) being supplied in an amount of from about 1,500 to 30,000, and preferably from about 3,000 to 15,000 s.c.f. (standard cubic feet) per barrel of total reactor feed, said feed including the intermediate fraction from catalytic cracking zone **11** entering by line **16** as well as recycle through line **31** from isomerization-cracking zone **19**, as hereafter described. Additional isomerization-cracking feed can be introduced into the system from an external source if desired. For example, light thermally cracked cycle oil from a refinery thermal cracking unit can be passed into isomerization-cracking zone **19** through lines **35**, **31** and **16** for conversion to gasoline. The present embodiment is based upon a total H_2 of approximately 6,000 s.c.f. per barrel of total feed.

The isomerization-cracking step is conducted as hereinbefore noted, i.e., a pressure of at least 500 p.s.i.g. and preferably from about 800 to 3000 p.s.i.g.; a temperature of between about 400° to 900° F., preferably 500° to 800° F.; an LHSV of from about 0.2 to 15, preferably about 0.4 to 3.0, and a catalyst meeting the requirements discussed above. The present process with feeds low in nitrogen (hydrofined) can be operated to advantage at a pressure of about 1500 p.s.i.g.; a space rate below about 2 LHSV; and an initial on-stream temperature of about 550° to 650° F., with progressive increase to about 750° to 850° F. With high-nitrogen feeds, similar conditions may be used, except that the temperatures during the on-stream period may be about 50° F. higher. As to the catalyst, the present design is based on data obtained with catalysts having molybdenum oxide (1% by weight Mo) deposited on a synthetic silica-alumina gel cracking support (containing approximately 87% silica and 13% alumina), or both cobalt oxide (2.3% Co) and molybdenum oxide (7.3% Mo), or cobalt (2.0% Co) and chromium (3.5% Cr), supported by the same type or silica-alumina gel.

The total effluent from the isomerization-cracking zone **19** is removed from that zone by line **22**. If the feed to zone **19** is one which contains nitrogen compounds, the reactor effluent will also contain ammonia due to the hydrogenation of the nitrogen compounds. These can be removed in the manner outlined in our copending application Serial No. 542,156. In any case, the effluent is cooled and passed by line **22** into a high pressure gas-liquid separator **23** from which a hydrogen-rich recycle stream is withdrawn overhead and returned, along with make-up hydrogen entering by line **21**, by line **20** to the isomerization-cracking zone. According to this particular design and feed, a hydrogen consumption of about 1200 to 1600 s.c.f. per barrel of fresh isomerization-cracking unit feed (360–470 s.c.f./bbl. based on the original gas oil feed to the catalytic cracking zone **11**) can be expected, thus requiring a corresponding amount of hydrogen to be added through line **21**. The remainder of the effluent is preferably passed by line **24** into a low pressure vapor-liquid separator **25** to remove C_4 and lighter normally gaseous components by line **26**. The remaining normally liquid portion of the effluent is then passed by line **27** into secondary fractionation zone **28** from which is recovered a relatively light gas fraction (C_4's and lighter) by lines **29** and **26**, a gasoline fraction (amounting to 3,000 b.p.d.)

by line 30, an intermediate fraction (1500 b.p.d.) boiling in the range of from about 400° to 475° F. by line 31, and a bottoms fraction boiling above about 475° F., amounting to about 1500 b.p.d., by line 32.

Following the above-noted separation step, the intermediate fraction is recycled as a component of the feed to the isomerization-cracking zone 19 by lines 31 and 16 wherein it undergoes further conversion to gasoline. The bottoms fraction recovered from fractionation zone 28 by line 32 can be diverted from the system by line 33 and employed as an excellent diesel (cetane number generally above about 45), jet, turbine, or other fuel where a low aromatics content is desirable, or processed further as desired.

RESULTS OBTAINABLE WITH PROCESS OF PRESENT INVENTION

With the particular design and feed stock described above, it can thus be expected to produce about 6500 b.p.d. (3500 b.p.d. from the catalytic cracking unit and 3000 b.p.d. from the isomerization-cracking unit) of gasoline of an octane number of around 96–100 F–1+3 ml. TEL. Further, about 1500 b.p.d. of excellent diesel fuel can be expected, thereby giving a total of about 8000 b.p.d. of valuable gasoline and diesel fuel.

To afford a means of comparison, from available data a process design was developed to cover the same basic two-reaction system except that the total bottoms (about 400° F.+initial boiling point) from the isomerization-cracking zone is recycled to the isomerization-cracking zone where it undergoes further reaction. Under such a scheme, a total gasoline production of 8000 b.p.d. (from a 10,000 b.p.d. fresh catalytic cracking feed) with a hydrogen consumption of about 1500–1700 s.c.f. per barrel of fresh isomerization-cracking unit feed (650–700 s.c.f./bbl. of original gas oil feed to the catalytic cracking zone 11) can be expected. However, even though the gasoline output in this latter case may be slightly more than the process of the present invention, the subject invention provides for about a 33 percent decrease in isomerization-cracking zone size and about a 45 percent reduction in the amount of hydrogen (based on the original catalytic cracking unit feed) necessary for the isomerization-cracking reaction. Obviously, these reductions are of considerable economic importance to the refiner who must meet the present day gasoline requirements of high compression engines at the lowest possible cost.

When operating the present process with recycle to the isomerization-cracking zone of the intermediate fraction recovered therefrom, and also with recycle to catalytic cracking zone 11 through line 18 of the fraction boiling above this intermdiate fraction, the following advantageous results are obtained. When operations are conducted in this manner, a total of about 7600 b.p.d. (4100 barrels produced in the catalytic cracking unit and 3500 b.p.d. in the isomerization-cracking unit) of high octane gasoline (around 96–100 F–1+3 ml. TEL), with a hydrogen consumption of about 1200–1600 s.c.f. per barrel of fresh isomerization-cracking process feed (500–670 s.c.f./bbl. based on original feed to the catalytic cracking unit 11), can be expected. Again, comparing these figures with the scheme wherein the total fraction from the isomerization-cracking unit boiling above gasoline is recycled to the catalytic cracking process, it can be seen that about a 21 percent reduction in isomerization-cracking unit size and about a 22 percent reduction in hydrogen consumption (based on gas oil feed to the catalytic cracking unit) can be expected.

We claim:

1. A process for upgrading hydrocarbon stocks having an initial boiling point of above about 325° F. and an end point below about 900° F., which comprises contacting said stocks in an isomerization-cracking zone, in the presence of from about 1,500 to 30,000 s.c.f. H_2 per barrel of total feed to said zone, with a catalyst comprising a hydrogenating-dehydrogenating component selected from the group consisting of (*a*) about 1 to 12% molybdenum oxilde, (*b*) a mixture of from about 1 to 12% molybdeum oxide and from about 0.1 to 10% cobalt oxide, (*c*) mixtures of from about 0.5 to 10% each of cobalt oxide and chromium oxide, (*d*) about 0.1 to 10% nickel metal, (*e*) about 0.1 to 10% nickel oxide, (*f*) about 0.1 to 10% nickel sulfide, (*g*) about 0.1 to 10% cobalt metal, (*h*) about 0.1 to 10% cobalt oxide, (*i*) about 0.1 to 10% cobalt sulfide, (*j*) mixtures of from about 0.1 to 10% each of nickel metal and cobalt metal, (*k*) mixtures of from about 0.1 to 10% each of nickel oxide and cobalt oxide, and (*l*) mixtures of from about 0.1 to 10% each of nickel sulfide and cobalt sulfide, said catalyst further comprising an active cracking support comprising silica-alumina having a silica content of about 70 to 99% at a temperature of from about 400° to 900° F., a pressure of at least 500 p.s.i.g., and an LHSV of from about 0.2 to 15; recovering from the effluent of said isomerization-cracking zone at least one normally gaseous fraction, at least one gasoline fraction, an intermediate fraction having an initial boiling point of about 375°±50° F. and an end point of about 475°±25° F., and a bottoms fraction boiling above said intermediate fraction; returning to the isomerization-cracking zone at least a portion of said intermediate fraction; and passing to a catalytic cracking zone at least a portion of said bottoms fraction.

2. The process of claim 1, wherein the catalyst is characterized by a severity factor (SF) less than 2.0.

3. A process for upgrading hydrocarbon stocks having an initial boiling point of above about 325° F. and an end point below about 900° F., which comprises contacting said stocks in an isomerization-cracking zone, in the presenec of from about 1,500 to 30,000 s.c.f. H_2 per barrel of total feed to said zone, with a catalyst comprising a hydrogenating-dehydrogenating component selected from the group consisting of (*a*) about 1 to 12% molybdenum oxide, (*b*) a mixture of from about 1 to 12% molybdenum oxide and from about 0.1 to 10% cobalt oxide, (*c*) mixtures of from about 0.5 to 10% each of cobalt oxide and chromium oxide, (*d*) about 0.1 to 10% nickel metal, (*e*) about 0.1 to 10% nickel oxide, (*f*) about 0.1 to 10% nickel sulfide, (*g*) about 0.1 to 10% cobalt metal, (*h*) about 0.1 to 10% cobalt oxide, (*i*) about 0.1 to 10% cobalt sulfide, (*j*) mixtures of from about 0.1 to 10% each of nickel metal and cobalt metal, (*k*) mixtures of from about 0.1 to 10% each of nickel oxide and cobalt oxide, and (*l*) mixtures of from about 0.1 to 10% each of nickel sulfide and cobalt sulfide, said catalyst further comprising an active cracking support comprising silica-alumina having a silica content of about 70 to 99% at a temperature of from about 500° to 800° F., a pressure of at least 500 p.s.i.g., and an LHSV of from about 0.4 to 3.0; recovering from the effluent of said zone a hydrogen-rich, gaseous fraction, a remaining normally gaseous fraction, at least one gasoline fraction, an intermediate fraction having an initial boiling point above about 325° F. and an end point of about 475°±25° F., and a bottoms fraction boiling above said intermediate fraction; returning to the isomerization-cracking zone said hydrogen-rich fraction and at least a portion of said intermediate fraction; and passing to a catalytic cracking zone at least a portion of said bottoms fraction.

4. A process for producing gasoline from a hydrocarbon fraction suitable for use as a feed to a catalytic cracking process, which comprises contacting said fraction with an active cracking catalyst in a catalytic cracking zone under cracking conditions; recovering from the effluent of said cracking zone at least one gas fraction, at least one gasoline fraction, an intermediate fraction having an initial T.B.P. above about 325° F. and an end point below about 900° F., and at least one fraction

boiling above said intermediate fraction; contacting said intermediate fraction in an isomerization-cracking zone, in the presence of from about 1,500 to 30,000 s.c.f. H_2 per barrel of total feed to said isomerization-cracking zone, with a catalyst comprising a hydrogenating-dehydrogenating component selected from the group consisting of (*a*) about 1 to 12% molybdenum oxide, (*b*) a mixture of from about 1 to 12% molybdeum oxide and from about 0.1 to 10% cobalt oxide, (*c*) mixtures of from about 0.5 to 10% each of cobalt oxide and chromium oxide, (*d*) about 0.1 to 10% nickel metal, (*e*) about 0.1 to 10% nickel oxide, (*f*) about 0.1 to 10% nickel sulfide, (*g*) about 0.1 to 10% cobalt metal, (*h*) about 0.1 to 10% cobalt oxide, (*i*) about 0.1 to 10% cobalt sulfide, (*j*) mixtures of from about 0.1 to 10% each of nickel metal and cobalt metal, (*k*) mixtures of from about 0.1 to 10% each of nickel oxide and cobalt oxide, and (*l*) mixtures of from about 0.1 to 10% each of nickel sulfide and cobalt sulfide, said catalyst further comprising an active cracking support comprising silica-alumina having a silica content of about 70 to 99% at a temperature of from about 400° to 900° F., a pressure of at least 500 p.s.i.g., and an LHSV of from about 0.4 to 3.0; recovering from the effluent of said isomerization-cracking zone at least one gas fraction, at least one gasoline fraction, an intermediate fraction having an initial T.B.P. above about 325° F. and an end point of about 475°±25° F., and a bottoms fraction boiling above said intermediate fraction; returning to the isomerization-cracking zone at least a portion of the intermediate fraction recovered from the effluent therefrom; passing to the catalytic cracking zone at least a portion of the bottoms fraction recovered from the effluent therefrom.

5. The process of claim 4, wherein a hydrogen-rich, normally gaseous fraction is recovered from the effluent of the isomerization-cracking zone and is returned as recycle to that zone.

6. The process of claim 4, wherein the catalyst in the isomerization-cracking zone is characterized by a severity factor (SF) below 2.0.

7. The process of claim 4, wherein a hydrocarbon fraction having an initial T.B.P. about about 325° F. and an end point below about 900° F., and obtained from a thermal cracking unit, is additionally passed into the isomerization-cracking zone.

8. A process for producing gasoline from a petroleum fraction suitable for use as a feed to a catalytic cracking process, which comprises contacting said fraction with an active cracking catalyst in a catalytic cracking zone under cracking conditions; recovering from the effluent of said cracking zone a gas fraction, at least one gasoline fraction, an intermediate fraction having an initial T.B.P. above about 325° F. and an end point below about 900° F., and at least one heavy fraction boiling above said intermediate fraction; returning at least a portion of said heavy fraction to the catalytic cracking zone; contacting said intermediate fraction in an isomerization-cracking zone, in the presence of from about 3,000 to 15,000 s.c.f. H_2 per barrel of total feed to said isomerization-cracking zone, with a catalyst comprising a hydrogenating-dehydrogenating component selected from the group consisting of (*a*) about 1 to 12% molybdenum oxide, (*b*) a mixture of from about 1 to 12% molybdenum oxide and from about 0.1 to 10% cobalt oxide, (*c*) mixtures of from about 0.5 to 10% each of cobalt oxide and chromium oxide, (*d*) about 0.1 to 10% nickel metal, (*e*) about 0.1 to 10% nickel oxide, (*f*) about 0.1 to 10% nickel sulfide, (*g*) about 0.1 to 10% cobalt metal, (*h*) about 0.1 to 10% cobalt oxide, (*i*) about 0.1 to 10% cobalt sulfide, (*j*) mixtures of from about 0.1 to 10% each of nickel metal and cobalt metal, (*k*) mixtures of from about 0.1 to 10% each of nickel oxide and cobalt oxide, and (*l*) mixtures of from about 0.1 to 10% each of nickel sulfide and cobalt sulfide, said catalyst further comprising an active cracking support comprising silica-alumina having a silica content of about 70 to 99% at a temperature of from about 500° to 800° F., a pressure of from about 800 to 3,000 p.s.i.g., and an LHSV of from about 0.4 to 3.0; recovering from the effluent of said isomerization-cracking zone a hydrogn-rich gaseous fraction, a remaining normally gaseous hydrocarbon fraction, a gasoline fraction, an intermediate fraction having an initial T.B.P. above about 325° F. and an end point below about 500° F., and a bottoms fraction boiling above said intermediate fraction; returning to the isomerization-cracking zone the hydrogen-rich fraction and at least a portion of and intermediate fraction recovered from the effluent from said zone; passing to the catalytic cracking zone at least a portion of the bottoms fraction recovered from the effluent from said zone.

9. The process of claim 8, wherein the catalyst in the isomerization-cracking zone is characterized by a severity factor (SF) below 2.0.

10. A process for producing gasoline from cracked petroleum stocks having initial boiling points above about 325° F. and end points below about 900° F., which comprises contacting said stocks in an isomerization-cracking zone, in the presence of from about 1,500 to 30,000 s.c.f. H_2 per barrel of total feed to said zone, with a catalyst comprising a hydrogenating-dehydrogenating component selected from the group consisting of (*a*) about 1 to 12% molybdenum oxide, (*b*) a mixture of from about 1 to 12% molybdenum oxide and from about 0.1 to 10% cobalt oxide, (*c*) mixtures of from about 0.5 to 10% each of cobalt oxide and chromium oxide, (*d*) about 0.1 to 10% nickel metal, (*e*) about 0.1 to 10 nickel oxide, (*f*) about 0.1 to 10% nickel sulfide, (*g*) about 0.1 to 10% cobalt metal, (*h*) about 0.1 to 10% cobalt oxide, (*i*) about 0.1 to 10% cobalt sulfide, (*j*) mixtures of from about 0.1 to 10% each of nickel metal and cobalt metal, (*k*) mixtures of from about 0.1 to 10% each of nickel oxide and cobalt oxide, and (*l*) mitxures of from about 0.1 to 10% each of nickel sulfide and cobalt sulfide, said catalyst further comprising an active cracking support comprising silica-alumina having a silica content of about 70 to 99% at a temperature of from about 500° to 800° F., a pressure of at least 500 p.s.i.g., and an LHSV of from 0.2 to 15; recovering from the effluent of said zone a hydrogen-rich gaseous fraction, a remaining normally gaseous fraction, at least one gasoline fraction, an intermediate fraction having an initial boiling point above about 325° F. and an end point below about 500° F., and a bottoms fraction boiling above said intermediate fraction; returning to the isomerization-cracking zone the hydrogen-rich fraction and at least a portion of the intermediate fraction recovered therefrom; passing to a catalytic cracking zone at least a portion of said bottoms fraction recovered therefrom.

11. The process of claim 10, wherein the feed to the isomerization-cracking zone is a catalytically cracked stock.

12. The process of claim 10, wherein the feed to the isomerization-cracking zone is a thermally cracked stock.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,135,682 June 2, 1964

Harold F. Mason et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 61, for "of" read -- to --; column 4, line 14, for "charactertics" read -- characteristics --; line 18, for "iso normal" read -- iso/normal --; line 32, for "aromatic" read -- aromatics --; line 64, for "iso normal" read -- iso/normal --; column 5, line 8, for "oxide or" read -- nickel oxide or --; line 11, for "hydrogenerating" read -- hydrogenating --; same column 5, line 62, for "cases" read -- case --; column 6, in the table, Case II, line 4 thereof, for "6,66" read -- 6,660 --; same table, Case I, line 12 thereof, for "1,50" read -- 1,500 --; column 9, line 53, for "intermdiate" read -- intermediate --; column 10, line 4, for "oxilde" read -- oxide --; line 5, for "molybdeum" read -- molybdenum --; same column 10, line 36, for "presenec" read -- presence --; column 12, line 8, for "hydrogn" read -- hydrogen --; line 15, for "of and intermediate" read -- of the intermediate --; line 36, for "10" read -- 10% --; column 12, line 43, for "mitxures" read -- mixtures --.

Signed and sealed this 10th day of November 1964.

(SEAL)
Attest:

ERNEST W. SWIDER
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